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(54) **Polyurethanes and thin walled elastic articles thereof**

(57) A polyurethane has mechanical properties close to those of natural rubber, in particular an S100 of less than 2.0 MPa, an elongation at break of at least 800%, and a tensile strength of above 16 MPa. Thin-walled articles such as condoms and gloves are made of films of the polyurethane. A polyurethane having the required properties may be obtained from a polymer diol, a diisocyanate and a glycol extender in which the polymer diol has a low content of monohydric material.

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POLYURETHANES AND THIN WALLED ELASTIC ARTICLES
THEREOF

This invention relates to a polyurethane and to thin walled elastic articles thereof.

Many devices for biomedical applications require the use of soft thin walled elastic articles. Examples of such articles are gloves for surgical operations and examinations under clean room conditions, and balloons for catheters and condoms. Natural rubber from latex is currently the material of choice for these types of applications due to its outstanding balance of mechanical properties. Typical properties are high elongation at break (800-900%), low modulus [a modulus at 100% elongation of 0.7 -0.9 MPa], acceptable tensile strength (20 - 35 MPa) and a low degree of creep. Natural rubber does, however, have the drawback that the presence therein of proteins and other undesirable compounds, such as vulcanisation accelerator residues, can lead to human allergic reactions if these compounds are leached from the rubber network during use. Another potential hazard is the formation of nitrosamines which are suspect carcinogens. It would therefore be beneficial to replace natural rubber with a synthetic elastomer for the fabrication of articles for biomedical applications.

Polyurethanes have been used to fabricate thin walled elastic articles, usually by dip coating from organic solvent based solutions. However, these solutions are usually quite viscous, due to the high molecular weight of the polymers, and this often presents problems with processing. The molecular weight of a polyurethane elastomer is a key parameter to performance, particularly in regard to the physical properties of the material which will be poor if a suitably high molecular weight is not attained.

Quite apart from these general problems of using polyurethanes to fabricate thin walled elastic articles, there are further difficulties in using them as a replacement for natural rubber. Whilst, in general, polyurethane films can be made of good tensile strength (e.g. 30 to 60MPa) and moderate elongation (450-650%), these known materials are much harder than natural rubber and will normally have a significantly higher modulus at 100% extension (hereinafter "S100"), for example of at least 2.2 and often much higher. Attempts to make softer polyurethanes have resulted in a lower modulus, but tensile strength and elongation at break have also been reduced and, most importantly, there has been an unacceptable loss in elasticity. Thus, it has not been possible to date to provide a polyurethane dipped film whose physical properties have been close to those of natural rubber.

We have now devised a polyurethane with properties close to those of natural rubber whereby thin walled elastic articles made of the polyurethane have very similar characteristics to such articles made of natural rubber.

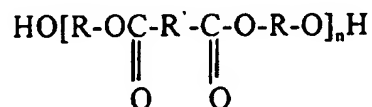
In one aspect, the invention provides a linear polyurethane having an S100 of less than 2.0 MPa, an elongation at break of at least 800% and a tensile strength of above 16 MPa.

The invention also includes a film of the polyurethane.

The invention further includes a soft thin-walled elastic article made of a polyurethane of the invention.

As used herein, the term "polyurethane" includes "polyurethane-urea".

The polyurethanes of the invention are linear and are made from one or more isocyanates, one or more polyols and one/ or more chain extenders. The preferred polyol is a polymeric diol i.e. a material which is polymeric and has two hydroxyl groups, located at the chain ends. Although polymeric, these materials are generally of limited molecular weight, typically ranging from 400 to 12,000 daltons. The chemical nature of these polyols is generally, but not exclusively, based upon polyester or polyether backbones. Thus a typical polyester polyol, usually prepared by polyesterification using an excess of diol, would have a general formula such as:



A polyether polyol, usually prepared by ring opening polymerization, would have a general formula: $\text{HO}[\text{RO}]_n \text{H}$.

The polyurethanes of the invention can be made either by the so-called "one-shot" bulk polymerisation method, or by chain extending prepolymers. The general method of preparation of the novel polyurethanes is conventional and, as such, will be well known to those skilled in the art. In general, we prefer to use the prepolymer method because it provides good control over hard/soft segment proportions and over product quality.

The choice of polyol is important, and we prefer to use α , ω -dihydroxy polyols. Examples of polyether polyols include poly-(propylene glycol)s (which we prefer), poly(tetramethylene glycol)s and poly(ethylene glycol)s. Additionally, α , ω -hydroxy polyester polyols may be used, examples including poly(ethylene adipate) diol, poly(butylene adipate) diol, poly(hexamethylene adipate) diol and copolymers of the above.

As stated previously, in order to achieve good physical properties in polyurethanes, high molecular weights are needed. It has been recognised in the art that α,ω -hydroxy polyols sometimes contain monohydroxy terminated species (called "monols") as impurities. These monols have only one hydroxy terminal and prevent the formation of high molecular weight products. The occurrence of monols in polyols can be reduced by using certain organometallic catalysts in the preparation, so that the polyol has only about 0.02 milliequivalents/g of unsaturation, but even this low level is not without effect. According to a preferred feature of the present invention, we prefer to use α,ω -hydroxy polyols which contain no more than about 0.01, and most preferably no more than about 0.007, milliequivalents unsaturation per gram. Materials of this specification are available commercially. For example, Arco Chemical Co. (USA) supply "Acclaim" polyols which are said to have a very low level of monol impurity. These "Acclaim" polyols are for use in making high performance cast polyurethane elastomers to meet requirements not met by conventional rubbers and plastics, e.g. to provide high performance flexibility and toughness. Their utility in the present invention, in contributing to the production of polyurethanes closely matching natural rubber, is quite different from their proposed use for cast polyurethanes and, indeed, it is surprising that they are useful for the quite different purpose of the present invention.

We prefer to use aliphatic diisocyanates to make the polyurethanes of the invention, since aromatic diisocyanates tend to give products of too high stiffness and creep to match natural rubber. Among the aliphatic diisocyanates which can be used is 4,4'-methylenebis(cyclohexyl isocyanate) (HMDI), available commercially as Desmodur W from Bayer. Others include isophorone diisocyanate (3-isocyanatomethyl-3,5,5-trimethylcyclohexyl isocyanate IPDI), available from Veba; hexamethylene

diisocyanate (HDI) available from Bayer; cyclohexane-1,4- diisocyanate (CHDI) available as a development product from AKZO; cyclohexane-1,4-bis(methylene isocyanate) (BDI) available as a development product from Eastman; 1,3-bis (isocyanatomethyl)cyclohexane (HXDI) available from Takeda; TMDI, a mixture of 1,6-diisocyanato-2,2,4,4-tetramethylhexane and 1,6-diisocyanato-2,3,4-trimethylhexane available from Veba; and the meta and para isomers of tetramethylxylene diisocyanate which are available as TMXDI from American Cyanamid.

The most preferred diisocyanates are alicyclic diisocyanates such as, for example, 4,4'-methylenebis(cyclohexyl isocyanate) available as Desmodur W.

Not only are aliphatic diisocyanates preferred for the purpose of making polyurethanes closely matching natural rubber, they are also preferred because the polyurethanes so formed are non-yellowing. This is an advantage with soft thin walled elastic articles.

In general, the isocyanates used in the present invention are bifunctional (i.e. diisocyanates) and are of sufficient reactivity to give the desired high molecular weight polyurethanes, with the desired elasticity. The optimum choice of isocyanate will, of course, depend on the choice of polyol and of chain extender, and the proportions used, as will be clear to those skilled in the art. In the case of poly(propylene glycol) diols, and butanediol as chain extender, we prefer to use Desmodur W as the isocyanate.

The nature of the chain extender can vary quite widely. We prefer to use bifunctional compounds, i.e. diols, and suitable examples include ethane-1,2- diol, propane-1,2-diol, propane-1,3-diol, butane-1,4-diol, hexane-1,6-diol, 2,3-dimethylbutane-2,3-diol, 2,5-dimethylhexane-2,5-diol. A preferred chain extender is butane-1,4-diol. In addition, diamines and hydroxyamines may be used as chain extenders to generate

poly(urethane-ureas). Examples of such chain extenders are ethylenediamine, propane-1,3-diamine, propane-1,2-diamine, butane-1,4-diamine, 2-methylpentane-1,5-diamine, hexane-1,6-diamine, ethanolamine, 1-aminopropan-2-ol, 3-aminopropan-1-ol, 2-aminopropan-1-ol, 2-aminobutan-1-ol and 4-aminobutan-1-ol. Use of amino compounds to prepare poly(urethane ureas) can have the drawback of restricting the solubility of the polymer to highly polar high boiling solvents such as dimethylformamide (DMF), N-methylpyrrolidone (NMP) and dimethyl sulphoxide (DMSO).

The proportions of isocyanate, and polyol and chain extender which are used will, of course, affect the proportions of hard and soft segments in the polyurethane, and the molecular weight. In general, the ratio hard:soft segment will be from 20:80 to 40:60.

The preferred method of preparation involves first reacting n mole equivalents of a polyol with $n+1$ mole equivalents of a diisocyanate to form a prepolymer. Thus, the weight ratios of polyol to diisocyanate will depend on the molecular weights of the reactants. By way of an example, if 1 mole equivalent of a polyol of molecular weight 2,000 is reacted with 2 mole equivalents of a diisocyanate such as HMDI of molecular weight 262, then the weight ratio of polyol to diisocyanate in the prepolymer is slightly less than 4 to 1. If the prepolymer is then extended with 1 mole equivalent of a diol, such as butanediol (molecular weight 90), the overall weight percentages of components in the final polyurethane will be 76% polyol, 20% diisocyanate, 4% extender. By way of a further example, if 2 mole equivalents of the same polyol are reacted with 3 mole equivalents of the same diisocyanate, the weight ratio of polyol to diisocyanate in the prepolymer will be approximately 5.1 to 1. If this prepolymer is now extended with 2 mole equivalents of the same diol and 1 mole equivalent of the same diisocyanate, then the overall weight percentages of components in

the final polyurethane will also be 76% polyol, 20% diisocyanate and 4% extender.

The number average molecular weights (M_n) of the polyurethanes of the invention will generally be in the range 90 to 150kg/mole, preferably from 100 to 120. The spread of molecular weight as determined by the ratio $M_w:M_n$ is generally from 1.2 to 2.2, preferably 1.4 to 1.8. (M_w is the weight average molecular weight.) As will be clear to those skilled in the art, the molecular weight of the polyurethane can be controlled by routine measures in the production process.

The polyurethanes of the present invention are closely matched to natural rubber in tensile properties. In this connection, the polyurethanes will generally have a S100 of less than 2.0MPa, and most preferably less than 1.0MPa, an elongation at break of at least 800%, and preferably above 1000%, and a tensile strength of above 16MPa, and most preferably above 20MPa. Polyurethanes with these particular combinations of properties so that they can be used in place of natural rubber, are novel.

Films of the invention are preferably made from organic solvent solutions of the polyurethanes, in conventional fashion such as by casting or dip coating. Any suitable organic solvent can be used but we generally prefer to use tetrahydrofuran, although butan-2-one, γ -butyrolactone or aprotic solvents such as dimethyl formamide, dimethyl acetamide and N-methyl pyrrolidone may be used depending on the polyurethane structure. The aprotic solvents can be used in conjunction with a small amount of an inorganic halide such as 1 to 3% of lithium bromide. Alternatively, a small proportion of a non-solvent for the polyurethane may be used in conjunction with an appropriate solvent; these may include acetone, methyl isobutyl ketone, methylene chloride and chloroform, for example. The solutions can vary in the solids content but, for making articles such as gloves or condoms, the solids contents will usually be from about 10 to 30%, more usually from

15 to 20%. Films of the invention normally have a thickness of from 20 to 250 μm , preferably 35 to 150 μm for condoms and 100 to 200 μm for gloves.

The production of polyurethanes with the unique combination of properties described is surprising. It would have been expected in the art that at the level of hard segment content used in the present invention, the resulting polyurethane would be much harder and of lower elongation at break than has actually been found. The combination of properties which are actually found is surprising and highly advantageous in its close match to the properties of natural rubber.

In order that the invention may be more fully understood, the following Examples are given by way of illustration only.

EXAMPLE 1

A polyurethane of the invention was made by the prepolymer method by taking 198g of a polypropylene glycol (Acclaim 2200), having a molecular weight of 1975 and a monol content of 6.2×10^{-3} milliequivalents per gram, and reacting it with 52.8g of HMDI at 55-60°C in the presence of 0.2g dibutyl tin dilaurate as catalyst. After a reaction time of 2 hours, a determination for the isocyanate content of the reaction mixture was made by a standard back titration of dibutylamine. The result of the NCO titration (approximately half that of the 6.7% by weight in the original reaction mixture) is used to determine the weights of chain extenders to be added to complete the reaction. Thus, 12.1g of butanediol and 17.6g of HMDI (a 2:1 molar ratio) were added to the reaction mixture which was heated and stirred until the reaction exotherm had reached 93°C. At this time the reaction mixture was poured into teflon coated trays and the polymer allowed to cure for 3 hours at 110°C.

The resulting polyurethane had 29% overall hard segment, M_n 131kg/mol and $M_w:M_n$ 1.5. The mechanical properties of a dipped thin film were 17.2MPa tensile strength, 1.2MPa S100, and 1330% elongation at

break. The solution had a viscosity of 250 cps and a solids content of 18%.

EXAMPLE 2

An equivalent polyurethane based on a conventional polypropylene glycol was prepared by reacting 225g of polypropylene glycol (ex Aldrich Chemicals) having a molecular weight of 2015, monol content of 0.045 milliequivalent per gram, with 58.7g of HMDI. The reaction was carried out for 2 hours at 60°C in the presence of dibutyl tin dilurate as catalyst. After carrying out an isocyanate determination, the prepolymer was then chain extended with 18.3g butanediol and 26.6g HMDI (in the molar ratio of 2:1 respectively). The reaction was allowed to exotherm to 95°C whereupon the polymer was poured into teflon coated trays and cured at 110°C for 3 hours.

The resulting polyurethane had 30% hard segment, M_n of 34kg/mole and $M_w:M_n$ of 1.89. The mechanical properties of a dipped thin film were 4.5MPa tensile strength, 2.4MPa S100 and 620% elongation at break. Thus, the value of using a polyol with low monol end group impurities is clearly demonstrated from the above examples.

EXAMPLE 3

Another polyurethane was prepared using the same reactants as in Example 1 except that ethylene glycol was substituted for butanediol as a chain extender. In this case, 202g of polyol was reacted with 52.2g of HMDI at 55-60°C to form a prepolymer. After carrying out an isocyanate determination, the prepolymer was extended by adding 11.6g of ethylene glycol and 24.6g of HMDI, the reaction conditions being the same as those in Example 1.

The resulting polyurethane had M_n 125kg/mole and $M_w:M_n$ of 1.5. The mechanical properties of a dipped thin film of this material were 29.5MPa tensile strength, 1.23MPa S100 and 920% elongation at break.

EXAMPLE 4

A polyurethane-urea was prepared using the same reactants as in Example 1

but ethanolamine was substituted for butanediol as a chain extender. 280.8g of polyol was reacted with 74.6g of HMDI at 60°C to form a prepolymer. After carrying out an isocyanate determination, the prepolymer was extended by adding 8.5g of ethanolamine to the reaction mixture and continuing stirring until the reaction exotherm had reached 100°C. The reaction mixture was then transferred to Teflon-coated trays and allowed to cure at 110°C for 3 hours.

The resulting polyurethane urea had 23% hard segment, M_n 109 kg/mol and M_w/M_n 1.6. The mechanical properties of a thin film, dipped from a 9% w/w solution of this material in THF, were 31 MPa tensile strength, 1.4 MPa S_{100} and 1020% elongation at break. The solution had a viscosity of 100 cP at a concentration of 15% w/w.

EXAMPLE 5

Higher molecular weight polyols can also be used to synthesize polyurethanes of the invention. A polyurethane of this type was prepared by taking 291.7g of polypropylene glycol (Acclaim 3200), having a molecular weight of 2967 and a monol content of 5×10^{-3} milliequivalents per gram, and reacting it with 77.35g of HMDI in the presence of 0.1g of dibutyl tin dilaurate. In this case a large excess of HMDI was used (3:1 molar ratio) to ensure that the higher molecular weight polypropylene glycol used would react completely to form an isocyanate capped prepolymer.

After a reaction time of 3 hours at 60°C, the isocyanate content of the reaction mixture was found to have decreased from 6.7% to 4.0%. The prepolymer was then extended by addition of 15.4g of butane diol and the reaction mixture stirred until the temperature had reached 90°C, whereupon

the polymer was transferred to Teflon-coated trays and cured at 110°C for 5 hours.

The resulting polyurethane had 24% hard segment, M_n of 146 kg/mole and M_w/M_n of 1.5. The tensile properties of a thin film, dipped from a 15% solution of this material in THF, having a viscosity of 535 cP, were found to be 21 MPa tensile strength, 1.4 MPa S_{100} and 1120% elongation at break.

EXAMPLE 6

Aliphatic diisocyanates are preferred to aromatic diisocyanates to synthesize polyurethanes of the invention as the use of aromatic diisocyanates tends to produce harder (higher S_{100}) elastomers. This is illustrated by the following example. An aromatic polyether urethane was synthesized by reacting 196.8g (0.097 mole) of polypropylene glycol (Acclaim 2200) having a molecular weight of 2040, with a three-fold excess (75.6g, 0.302 mole) of diphenyl methane diisocyanate (MDI) at 65°C for 3 hours. This reaction was catalysed by the addition of 0.07g of dibutyl tin dilaurate. After carrying out an isocyanate determination, this prepolymer was diluted with 354g of THF and extended by addition of 16.94g (0.188 mole) of butane diol. The chain extension reaction was allowed to proceed at 60°C for 3 hours during which time a further 500g of THF was added to control the viscosity of the polymer solution. The molecular weight of the resulting polyurethane, having 30% hard segment, was M_n 81 kg/mol and M_w/M_n 1.9. The mechanical properties of a polyurethane film cast from the solution were 23.6 MPa tensile strength, 3.1 MPa S_{100} and 824% elongation.

Comparison of the mechanical properties of this elastomer with those of the polyurethane cited in Example 1 clearly demonstrates that use of an aromatic

diisocyanate (MDI) has produced a stiffer (higher S_{100}) material with lower elongation at break.

EXAMPLE 7

Thin-walled elastic articles, such as condoms, were made from the polyurethanes of Examples 1 to 3 as follows. Solutions were prepared of 15-20% total solids of these polymers, in a solvent such as tetrahydrofuran, at a viscosity of 500-600 cps measured at 30°C. The solutions were degassed and allowed to equilibrate at room temperature for 2 hours. The thin-walled article was made by dipping a glass mandrel into the solution and then removing the mandrel therefrom to form a solution coated mandrel. This is allowed to set in the solution vapour layer prior to final drying in an oven for a specified length of time. Once drying is complete, the coated glass mandrel is placed in a cool water tank and allowed to hydrate for 20 minutes. The resulting dried thin-walled article is then removed from the glass mandrel.

The above process generally applies to all solvent based dipping of a thin walled article using both conventional polyurethanes as well as the polyurethanes of the invention. However, a solution of a polyurethane of the invention will generally have a lower viscosity than a polyurethane synthesized from a conventional polyol (polypropylene glycol) of equivalent molecular weight and solids content. This allows for dipped articles to be produced where the formation of defects such as holes (from bubbling) and uneven film thickness is avoided.

CLAIMS:

1. A linear polyurethane having an S100 of less than 2.0 MPa, an elongation at break of at least 800% and a tensile strength of above 16 MPa.
2. A polyurethane according to claim 1, which has a number average molecular weight (M_n) of from 90 to 150 kg/mole.
3. A polyurethane according to claim 2, wherein M_n is from 100 to 120 kg/mole.
4. A polyurethane according to claim 1, 2 or 3, wherein the ratio $M_w:M_n$ is from 1.2 to 2.2.
5. A polyurethane according to claim 4, wherein the ratio $M_w:M_n$ is from 1.4 to 1.8.
6. A polyurethane according to any of claims 1 to 5, wherein S100 is less than 1.0 MPa.
7. A polyurethane according to any of claims 1 to 6, which has an elongation at break of greater than 1000%.
8. A polyurethane according to any of claims 1 to 7, which has a tensile strength of greater than 20 MPa.
9. A polyurethane according to any of claims 1 to 8 which comprises an α,ω -dihydroxy polyol.

10. A polyurethane according to claim 9, wherein the α,ω -dihydroxy polyol is a poly(propylene glycol).
11. A polyurethane according to claim 9 or 10, wherein the α,ω -dihydroxy polyol contains no more than 0.01 milliequivalents unsaturation per gram.
12. A polyurethane according to any of claims 1 to 11, which comprises an aliphatic diisocyanate.
13. A polyurethane according to claim 12, wherein the aliphatic diisocyanate is an alicyclic diisocyanate.
14. A polyurethane according to claim 13, wherein the diisocyanate is 4,4-methylenebis(cyclohexyl isocyanate).
15. A polyurethane to any of claims 1 to 14, which comprises a chain extender.
16. A polyurethane according to claim 15, wherein the chain extender is butane-1,4-diol.
17. A polyurethane according to any preceding claim wherein the ratio hard:soft segment is from 20:80 to 40:60.
18. An organic solvent solution of a polyurethane as claimed in any of claims 1 to 17.
19. A film of a polyurethane as claimed in any of claims 1 to 17.



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Patent
Office

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Application No: GB 9718276.0
Claims searched: 1-24

Examiner: Alan Kerry
Date of search: 20 November 1997

Patents Act 1977
Search Report under Section 17

Databases searched:

UK Patent Office collections, including GB, EP, WO & US patent specifications, in:

UK CI (Ed.O): C3R RSM, R32KC, R32KL

Int CI (Ed.6): C08G 18/48, 18/66

Other: Online databases: WPI, CLAIMS

Documents considered to be relevant:

Category	Identity of document and relevant passage	Relevant to claims
X	GB 2174709 A (MOBAY) - see Claim 4 and the Examples	1 at least
X	GB 2159526 A (GORE) - see the Examples, Table 2 V	1 at least
A	GB 1401986 (PPG) - see Claim 1 and Examples 5-17	1 at least
A	EP 0781791 A1 (BASF) - see Examples 3-7 and page 1, lines 26-34 and page 10, lines 30-39	1 & 11
X	EP 0741152 A1 (ARCO) - see Claim 1 and Examples 1-5	1 & 11
X	US 4917850 (GRAY) - see Claims 1, 3 & 5 and the Example	1 & 23 at least

X	Document indicating lack of novelty or inventive step	A	Document indicating technological background and/or state of the art.
Y	Document indicating lack of inventive step if combined with one or more other documents of same category.	P	Document published on or after the declared priority date but before the filing date of this invention.
&	Member of the same patent family	E	Patent document published on or after, but with priority date earlier than, the filing date of this application.